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Production of VOCs by Heterogeneous Oxidation Chemistry at the Sea Surface Microlayer of South China Sea

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Sea surface microlayer (SML) is ubiquitous in the environment and provides a unique medium for interfacial oxidation processing. Ozone oxidation chemistry on proxy compounds of SML generates volatile organic compounds (VOCs) in the atmosphere. To shed light on the proposed significance of this chemistry, we investigated the formation of VOCs through heterogenous ozone (O_3) oxidation chemistry with authentic SML collected at 10 different places located at coastal area of South China Sea and on sites which were located 110 and 130 km from the coast which can be considered as open sea. We present real-time measurements of VOCs produced by interfacial oxidation chemistry of gaseous O_3 with an authentic SML by using a Proton Transfer Reaction-Time of Flight-Mass Spectrometry (PTR-ToF-MS). The detected compounds were subsequently identified by Thermal Desorption-Gas Chromatography-Mass Spectrometry (TD-GC-MS) and High-Pressure Liquid Chromatography with UV detection based on the derivatization of the carbonyl compounds with 2,4-dinitrophenylhydrazine (NDPH-HPLC-UV).

We show that ozone oxidation chemistry at the SML can lead to a large suite of unsaturated and saturated CHO organic compounds in the marine air above the sea, including acetaldehyde, acetone, propanal, cyclohexanone, hexanal, heptanal, 2,4-dimethyl-1-heptene, octanal, 2-ethylhexanol, nonanal, and decanal. Based on the quantified product compounds we estimated the production rates of the compounds formed during the heterogenous ozonolysis of SML. The production rates of acetone and acetaldehyde were compared with their emission rates determined during cruise measurements in the oceans.

These results provide significant update to our understanding of abiotic formation of VOCs, indicating that ozone oxidation chemistry at SML may be a major source for VOCs production in particular ketones and saturated and unsaturated aldehydes in marine air of South China Sea which should be considered in future model studies.

Therefore, we strongly recommend model studies to consider this chemistry as an additional source of acetaldehyde and acetone, which can affect the O_3 and OH cycles in marine boundary layer. The produced unsaturated compounds by the suggested ozone oxidation chemistry at SML can affect the secondary organic aerosol (SOA) formation process in marine boundary layer.